

The Effect of Hypergol Exposure on Polycyanurate Matrix Composites

15 July 1995

Prepared by

T. J. DICKINSON
Space and Missile Systems Center
Air Force Materiel Command
United States Air Force



R. J. ZALDIVAR and R. W. KOBAYASHI
Mechanics and Materials Technology Center
Technology Operations

Prepared for

SPACE AND MISSILE SYSTEMS CENTER
AIR FORCE MATERIEL COMMAND
2430 E. El Segundo Boulevard
Los Angeles Air Force Base, CA 90245

19951122 055

Engineering and Technology Group

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED

DTIC QUALITY INSPECTED 1

This report was submitted by The Aerospace Corporation, El Segundo, CA 90245-4691, under Contract No. F04701-88-C-0089 with the Space and Missile Systems Center, Los Angeles Air Force Base, CA 90245. It was reviewed and approved for The Aerospace Corporation by S. Feuerstein, Principal Director, Mechanics and Materials Technology Center. Maj. J. W. Cole was the project officer for the Mission-Oriented Investigation and Experimentation (MOIE) program.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.



MAJ. J. W. COLE
SMC/SDE

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 15 July 1995		3. REPORT TYPE AND DATES COVERED
4. TITLE AND SUBTITLE The Effect of Hypergol Exposure on Polycyanurate Matrix Composites			5. FUNDING NUMBERS F04701-93-C-0094	
6. AUTHOR(S) T. J. Dickinson, R. J. Zaldivar, and R. W. Kobayashi				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The Aerospace Corporation Technology Operations El Segundo, CA 90245-4691			8. PERFORMING ORGANIZATION REPORT NUMBER TR-95(5935)-2	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Space and Missile Systems Center Air Force Materiel Command 2430 E. El Segundo Boulevard Los Angeles Air Force Base, CA 90245			10. SPONSORING/MONITORING AGENCY REPORT NUMBER SMC-TR-94-40	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (<i>Maximum 200 words</i>) Polycyanurates are a new class of thermosetting polymers having properties superior to those of epoxies for spacecraft applications. These polymers are gaining wide acceptance due to their lower moisture uptake, reduced outgassing, high glass transition temperature, and excellent resistance to thermally induced microcracks. Polycyanurate composites are being used in current satellite programs and will likely see increased applications in satellite and launch vehicles. It is necessary to determine the compatibility of these composites with spacecraft propellants. This study examines the compatibility between two hypergol rocket propellants (anhydrous hydrazine and nitrogen tetroxide) and polycyanurate composites composed of T-300 fibers and polycyanurate matrices derived from bisphenol A. The mechanical performance of polycyanurate composites was compared to T-300/934 epoxy composites, a current state-of-the-art system for these applications. Fiber and neat resin specimens were tested in addition to the composite systems. The tensile strength of the PAN-based T-300 fibers was not affected by 24-hour exposures in hydrazine and nitrogen tetroxide. The neat resin specimens were significantly affected by both fuel (anhydrous hydrazine) and oxidizer (nitrogen tetroxide), as witnessed by changes in mass, surface hardness, and tensile strength. Hydrazine dissolved the polycyanurate, but was absorbed by the epoxy. Nitrogen tetroxide attacked both resins, with degradation occurring twice as fast for the epoxy. Tensile strengths were determined for both exposed and unexposed specimens. Tensile strength decreases were observed to differing degrees for both of these composite systems as a function of propellant and exposure time. Scanning electron microscopy was also used to examine the fracture surfaces and microstructure of both systems before and after exposure.				
14. SUBJECT TERMS Polycyanurates, Propellant resistance, Propellant exposure			15. NUMBER OF PAGES 27	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT	

Preface

We would like to thank Ms. S. Genova and Mr. E. Fournier for their expertise and diligence in conducting the propellant exposures, Mr. M. Marcus for conducting the hardness tests, and Mr. D. Hanna for mechanical testing assistance. We would also like to thank Dr. C. Segal, Dr. S. Zacharius, and Dr. W. Kao for their leadership, technical insight, and suggestions. This study was made possible by the Air Force's engineering internship program with The Aerospace Corporation.

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

Contents

1. Introduction.....	1
2. Experimental.....	3
2.1 Materials and Processing.....	3
2.2 Propellants.....	5
2.3 Analysis.....	5
3. Results and Discussion.....	7
3.1 Pathfinder Results.....	7
3.2 Effects of Propellants on Carbon Fiber	8
3.3 Effects of Propellants on Neat Resin Coupons.....	9
3.4 Effects of Propellants on Composite Systems.....	17
4. Conclusions.....	21
References	23

Figures

1. The chemical structures of both the cyanate monomer and the cyclotrimerized prepolymer used in this study.....	3
2. The effect of various hydrazine fuel exposures on polycyanurate and epoxy resin mass changes (60-min exposure).	7
3. The effect of 24-h exposure condition on the tensile strength of T-300 carbon fiber.....	8
4. The effect of hydrazine exposure on polycyanurate and epoxy resin mass changes.	9
5. The effect of nitrogen tetroxide exposure on polycyanurate and epoxy resin mass changes.	10
6. The effect of nitrogen tetroxide and hydrazine exposure on polycyanurate dogbone specimens.	11

7. The effect of nitrogen tetroxide and hydrazine exposure on 934 epoxy dogbone specimens.....	12
8. Scanning electron micrographs of fracture surfaces of nitrogen tetroxide and hydrazine-exposed polycyanurate dogbone specimens.....	13
9. Scanning electron micrographs of fracture surfaces of nitrogen tetroxide and hydrazine exposed epoxy dogbone specimens.....	15
10. The effect of hydrazine exposure on polycyanurate and epoxy resin and composite samples.....	16
11. The effect of nitrogen tetroxide exposure on polycyanurate and epoxy resin and composite samples.....	16
12. Scanning electron micrographs of T-300/polycyanurate composite fracture surface as a function of exposure (a) control, (b) hydrazine exposed, (c) NTO exposed.....	18
13. Scanning electron micrographs of T-300/epoxy composite fracture surface as a function of exposure (a) control, (b) hydrazine exposed, (c) NTO exposed.....	19

Table

1. Test Matrix of Test Specimens Used for Each Exposure Condition.....	4
--	---

1. Introduction

Polycyanurate composite systems, due to their improved performance, are being introduced as a replacement for epoxy composites in many structural and space applications. Composites utilizing a polycyanurate matrix are superior to those with epoxy matrices due to their increased toughness and dimensional stability, lower moisture absorption, and reduced outgassing.¹

The cyanate ester monomers used in this study are bisphenol-A derivatives containing cyanate (OCN) functional groups. Upon heating, they undergo cyclotrimerization to form networks with triazine rings as crosslinks linked by bisphenol units. Resin and polycyanurate properties can be varied by changing the bisphenol linkage or aromatic ring substituents. The low cross-link density of these polymers allows a high degree of rotational freedom around ring couplings, producing a composite matrix of superior toughness. Since OH groups are also eliminated during monomer synthesis, the cured polymers exhibit low moisture absorption, approximately 2 to 3 times lower than typical epoxies, which contributes to high dimensional stability.

Polycyanurate composites are currently used on several satellite programs and are proposed for use on numerous other spacecraft. Current programs include the military's MILSATCOM, NASA's AXAF-1, and Clementine, as well as other commercial satellites. Programs considering these composites for future applications include the next generation of military early-warning satellites, space- and ground-based ballistic missile interceptors, Earth Observing System (EOS), Pluto Fast Flyby, and advanced bus and spacecraft structures under development by TRW and Boeing. Common satellite components utilizing polycyanurate composites are primary bus structures, tubes and struts, solar-array panels, metering trusses, optical benches, backing material for mirrors, and phased-array antennas.

Although quickly gaining popularity, polycyanurates are relatively new materials with a limited database. Since they are already being incorporated into space vehicles, it is imperative that we have a thorough understanding of how they will react in this unique environment. Hypergol rocket propellants are toxic and highly reactive substances. The most common fuels are hydrazine (N_2H_4) and its derivatives, with nitrogen tetroxide (N_2O_4) used as an oxidizer. Leakage of these propellants threatens the safety of personnel and hardware. This threat increases if materials with poor resistance to these propellants become contaminated, especially loaded structures such as pressurant tanks. The objective of this study was to determine the effects of hypergol rocket propellants on the mechanical and physical properties of polycyanurate composites and to compare these effects with those of a current state-of-the-art epoxy system. This material compatibility study will help assess the use of fiber-reinforced polycyanurate composites on future spacecraft and launch vehicles.

2. Experimental

2.1 Materials and Processing

The two thermoset polymers selected for this study are Ciba Geigy's AroCy B cyanate ester resin and ICI Fiberite's 934 epoxy resin. The AroCy B resin is a bisphenol A dicyanate, where the bisphenol linkage consists of an isopropyl group $[(CH_3)_2C]$ with single hydrogen atoms serving as aromatic ring substituents (Figure 1). The published tensile strength and modulus for the polycyanurate are 12.0 ksi and 0.47 Msi, respectively. The associated values for the epoxy are 12.0 ksi and 0.60 Msi. The reinforcing material selected for use in the composite systems is the T-300 PAN-based carbon fiber produced by Amoco Performance Products, Inc. All fibers used in this study were shear-treated and unsized, having a tensile strength of 530 ksi and tensile modulus of 33.5 Msi. Four types of test specimens were manufactured from these materials in this study: neat resin coupons, raw fiber tow bundles, impregnated unidirectional tow composites, and multiple-ply composite panels. This allowed for the examination of propellant effects on each component as well as on the combined composite system. The test matrix is shown in Table 1.

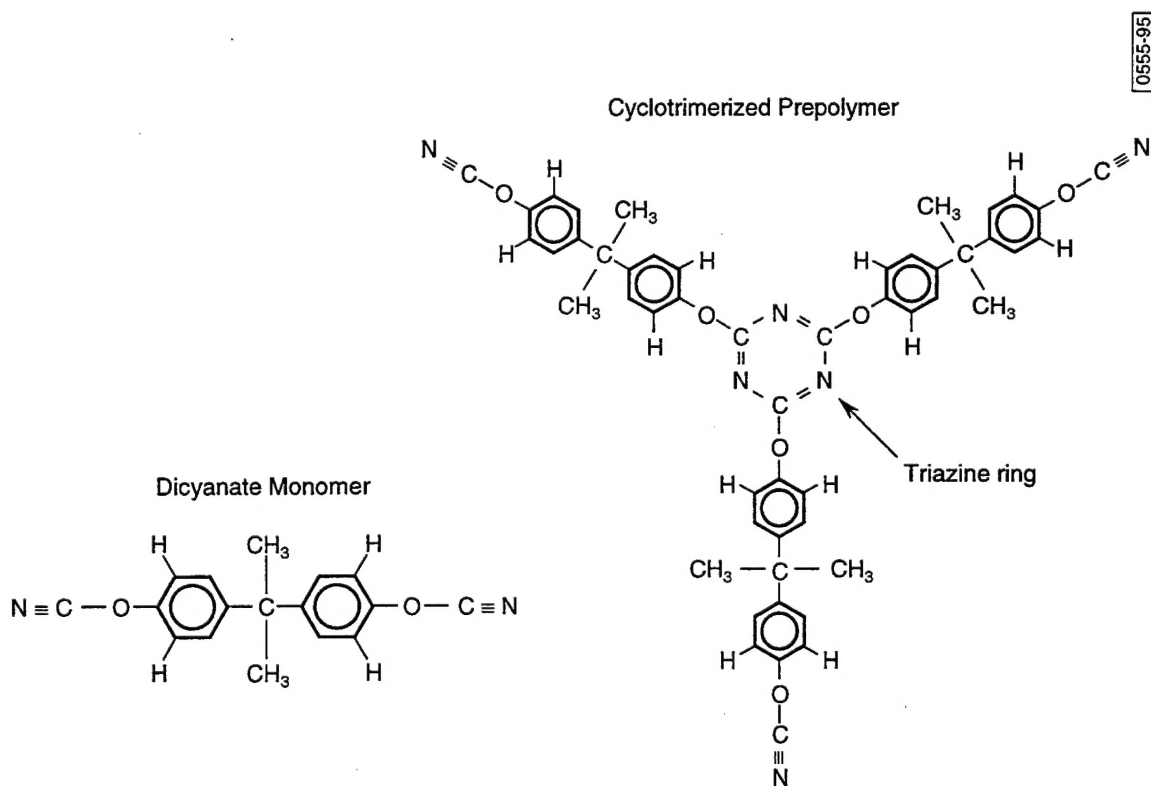


Figure 1. The chemical structures of both the cyanate monomer and the cyclotrimerized prepolymer used in this study.

Table 1. Test Matrix of Test Specimens Used for Each Exposure Condition

Specimen Type	Number of Test Specimens for Each Exposure Condition										
	Control	Hydrazine					Nitrogen tetroxide				
	0 min	2 min	5 min	30 min	1 h	24 h	30 min	1 h	2 h	5 h	24 h
Raw T-300 fiber	25					25					25
Polycyanurate resin coupons	10	5	5	5	5		5	5	5	5	
Epoxy resin coupons	10	5	5	5	5		5	5	5	5	
Polycyanurate composite tows	25	25	25	Not testable			na	na	25	25	
Epoxy composite tows	25	25	25	25	25		na	na	25	25	
Polycyanurate composite panels	10	5	5	na	na		na	na	5	5	

Neat resin coupons were produced by melting and casting each resin into Teflon® molds designed according to ASTM D 638, Type IV. Two molecular weight oligamers of dicyanate monomers were blended by YLA, Inc. The catalyst used is a cobalt acetyl acetonate mixture and accounts for 1.0 weight % of the total formulation. ICI Fiberite's 934 epoxy blend was supplied as a hot melt resin. A 15 wt.% solution of the resin in acetone was necessary to facilitate processing. The cyanate ester resin was processed at 120°C under a 30-in. Hg vacuum for 30 min to remove trapped air and volatiles. The epoxy resin was processed similarly, except that a total of 60 min was allowed for complete removal of the solvent. Both resins were cured in ambient air according to manufacturer's specifications. The AroCy B was cured at 177°C for 1 h with a final 2-h post cure at 232°C. The 934 epoxy was heated to 121°C for 4 h followed by a 2-h cure at 177°C. Upon cooling, the specimens were removed and machined to final dimensions. The resin dogbone gage width and thickness measured 0.25 in. and 0.12 in., respectively.

Raw fiber bundles and unidirectional tow composites were fabricated from T-300 fibers (3000 filaments/tow). Those with the cyanate ester resin matrix were provided as 55% resin content prepreg from YLA, Inc., using the same formulation as the neat resin. This prepreg was wound on a rack and placed in an oven for curing. Composites made with epoxy resin were solution impregnated at The Aerospace Corporation. The tow was first prepared by winding it on a rack and solution impregnating with a 30 wt.% solution of resin in acetone. The solvent was then allowed to evaporate in a fume hood overnight. With the prepreg free of solvent, the rack was placed in an oven for curing. All tows were subjected to the same cure cycles as the neat resin specimens. Upon cooling, the tows were cut to 5-in. lengths and removed from the rack. In order to isolate the effects of the propellants on the bare fiber, raw fiber bundles were also mounted and epoxy impregnated after undergoing exposure to the propellants.

Polycyanurate matrix composite panels were also fabricated. These panels were manufactured at The Aerospace Corporation and consisted of eight, 0.010-in.-thick layers arranged in a 0/+45/-45/0 balanced, symmetric orientation. The prepreg tape used for these panels was supplied by

YLA, Inc. with a resin content of 55% and the same formulation as the neat resin. After vacuum bag processing in a press at 50 psi and 177°C for 1 h, the panels were post-cured at 232°C for 5 h. Two panels were produced, and their fiber volumes were determined by optical microscopy to be 0.48 and 0.59. For purposes of mechanical data analysis, each fiber volume was normalized to 0.60. Specimens were cut from the panels and milled to the dimensions specified in ASTM D 3039.

2.2 Propellants

Several types of hydrazine fuels are commonly used on spacecraft, four of which were examined in this program: anhydrous hydrazine or hydrazine (N_2H_4), monomethylhydrazine or MMH, 1,1-dimethylhydrazine or UDMH, and Aerozine-50, a 50/50 by weight mixture of anhydrous hydrazine and UDMH. The most common spacecraft oxidizer, nitrogen tetroxide, was also selected. All propellants were used as supplied.

For purposes of this study, the most reactive of the four hydrazine fuels was selected for testing. A pathfinder test procedure, using mass and physical changes of exposed resin as selection criteria, was employed to make this determination. 100 mg cubes of each cured polymer were placed in vials and immersed in each of the four fuels. After exposure durations of 30 and 60 min, the specimens were rinsed with deionized water and allowed to dry in a fume hood for 72 h. The resin cubes were then re-weighed, and mass and dimensional changes were measured. Physical changes were also noted.

Test specimens were exposed to the propellants in several ways. For the raw fiber bundles, tow material was wrapped on two aluminum frames, with one immersed in hydrazine and the other in nitrogen tetroxide. All unidirectional tow composites were completely immersed in graduated cylinders containing fuel and oxidizer. Because of the rapid degradation of polycyanurate in hydrazine, the ends of the tows were protected by Apiezon® sealing compound to enable later application of mechanical testing tabs. Teflon holders were used for neat resin coupons and composite panels to minimize the use of propellants and corresponding hazardous waste. The ends of both specimen types were preserved with adhesive-backed Teflon tape; however, the gage section of each specimen remained completely immersed for the entire exposure duration. All specimens were rinsed with deionized water after exposure and allowed to dry in a fume hood for 48 h before further processing. Fuel exposures were conducted for up to 24 h; oxidizer exposures lasted as long as 72 h. The propellant exposure durations for each specimen type are indicated in Table 1.

2.3 Analysis

A mass loss or gain analysis was conducted on cured resin specimens exposed to the selected fuel and oxidizer. Polycyanurate and epoxy specimens were cut into 150-mg cubes and immersed in the propellants. After exposure, the specimens were rinsed with deionized water and allowed to dry in a fume hood. Each specimen was re-weighed after 24 h and again after 72 h in a fume hood. No further change in mass was detected for either polymer after the 72-h check.

Tensile testing was performed on neat resin coupons, unidirectional tows, and composite panels. The ends of both types of composites were bonded between tabs. The gage lengths for the resin coupons, tow, and panels were 1.0 in., 2.0 in., and 6.0 in., respectively. All samples were loaded to failure in a Universal Instron testing machine. The crosshead speed for the resin coupons and tows was 0.05 in./min while a speed of 0.10 in./min was used for the panels. The ultimate load was recorded for each sample and used to calculate tensile strength. A strain gage was attached to the resin coupons and composite panels to record tensile strain data, which was then used to calculate tensile modulus. All testing was conducted as specified in ASTMs D 638, D 3039, and D 4018 for the resin coupons, composite panels, and unidirectional tows, respectively.

Cross sections of the resin coupons were subjected to hardness testing to further examine the effects of the propellant penetration on the polymers. Samples were cast in Epon 815 epoxy and polished in preparation for testing. Knoop hardness numbers were calculated for nine points evenly spaced across the width of the gage sections. Scanning electron microscopy (SEM) was also used to analyze the microstructure and fracture surfaces of all specimens.

3. Results and Discussion

3.1 Pathfinder Results

An important indicator of chemical compatibility of a material is the change in mass that occurs as a result of exposure. For the polycyanurate, fuel exposures resulted in either no change or a considerable mass loss depending on the fuel, with a 42% mass loss after 60 min in anhydrous hydrazine being the most significant. However, epoxy specimens experienced either no change or a slight increase in mass due to absorption, with a 2% mass increase after 60 min in anhydrous hydrazine being the most significant (Figure 2). Physical changes in the resins and fuels were also noted. The polycyanurate specimens that were affected appeared to partially dissolve in the fuels, turning the fuels yellow in color with white particulates settling out of solution. The surfaces of the affected epoxy specimens became discolored, but the specimens maintained their original dimensions, and the fuels remained clear. For both polymers, anhydrous hydrazine had the most significant effect, both in mass and physical changes, followed by Aerozine-50 and MMH. UDMH essentially did not affect the mass or appearance of either polymer. As a result of this selection process, anhydrous hydrazine, hereafter referred to as "hydrazine," was the fuel chosen for testing.

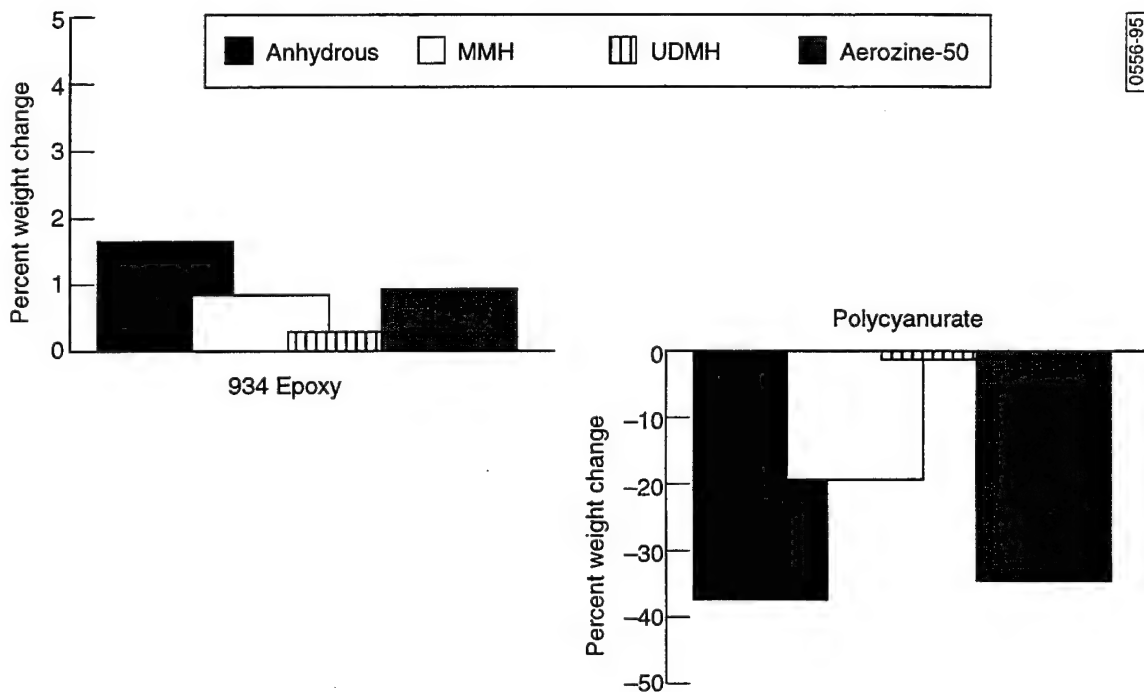


Figure 2. The effect of various hydrazine fuel exposures on polycyanurate and epoxy resin mass changes (60-min exposure).

3.2 Effects of Propellants on Carbon Fiber

Neither hydrazine nor nitrogen tetroxide affected the tensile strength of the T-300 fibers. The published strength of the fiber is 530 ksi. Calculated strength for control specimens was 490 ksi, or 92.5% of the published strength. For fibers exposed to fuel and oxidizer, strengths of 467 ksi and 495 ksi, respectively, were achieved. Exposed fiber strengths differ less than 5.0% from the strength of the control specimens as shown in Figure 3. These calculations are based on the assumption of 100% fiber strength utilization.

Micrographs obtained from the SEM were compared for the exposed and unexposed cases. No observable changes in the surface of the fibers were detected as the result of exposure to either propellant. Fracture surfaces of composite tows fabricated from exposed fiber were also compared with those from the control group. Analysis revealed the same amount of fiber pull out for both types of composites for all three conditions (unexposed, oxidizer exposed, and fuel exposed).

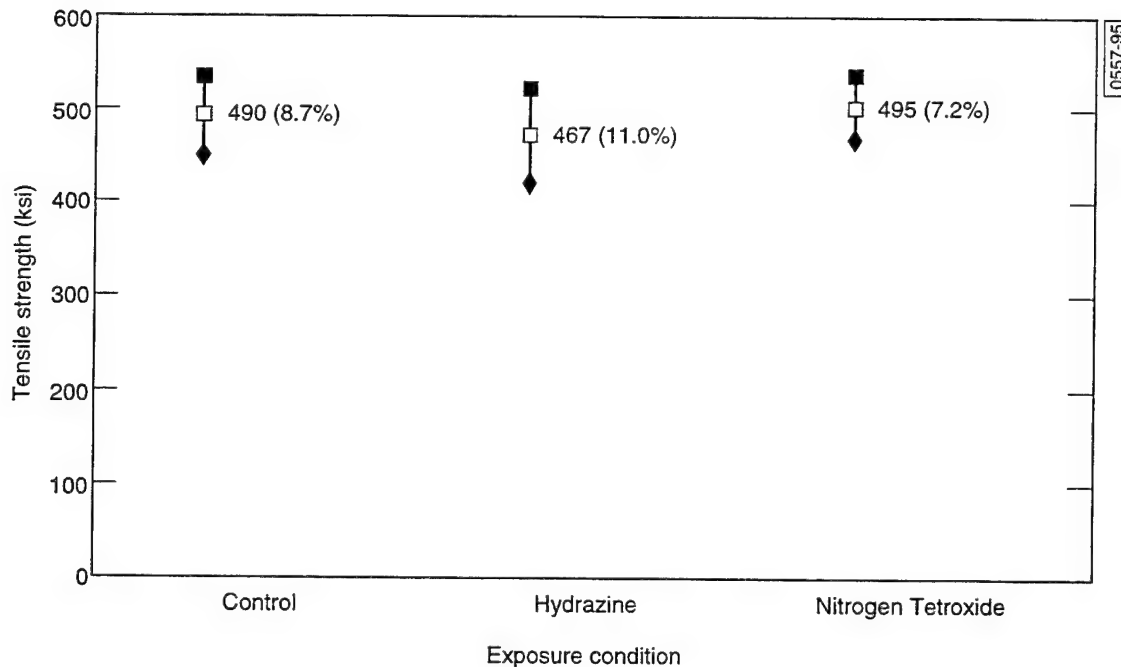


Figure 3. The effect of 24-h exposure condition on the tensile strength of T-300 carbon fiber.

3.3 Effects of Propellants on Neat Resin Coupons

The effect of fuel type and exposure time on mass gain or loss was conducted for both resin systems. Figure 4 shows a graph depicting the effect of hydrazine on the mass changes as a function of exposure time for both resin systems. As shown, the cured polycyanurate resin sample shows 95% mass loss within the first 2 h of exposure. The epoxy, however, does not show any significant variation in mass loss over a 24-h exposure time. This variation in chemical resistance is due to the inherent differences in the chemical structure of both polymers. The single bond between the carbon and oxygen atoms of the cyanate (OCN) functional group of the polycyanurate resin is a site that is highly susceptible to hydrolysis by a strong base. Even after formation of the triazine ring, this ether linkage is susceptible to reactions with a strong base such as hydrazine. Since this linkage is at a cross-link site, severing it will cause degradation of the polymer structure. On the other hand, such a weak link does not exist in the epoxy structure, which may explain the negligible changes in resin mass loss.

Figure 5 depicts the effect of nitrogen tetroxide on the mass changes as a function of exposure time for both resin systems. As shown, both systems show an initial increase in mass after 12 h exposure, after which both resins are completely dissolved. The epoxy was the first to dissolve, with only 5% of its original mass left after 32 h of exposure, compared to 72 h required to consume the same quantity of polycyanurate. It appears that the nitrogen tetroxide is initially more easily absorbed by the epoxy network, initiating a mechanism by which the epoxy is more rapidly consumed than the polycyanurate resin. This variation in rate may also be due to the

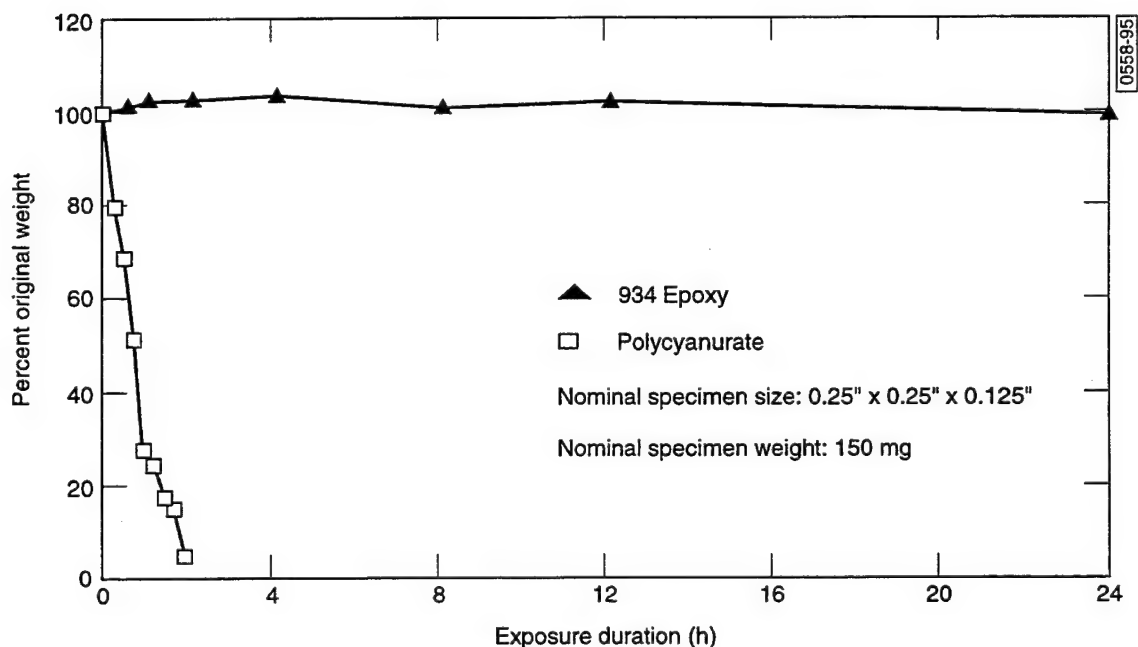


Figure 4. The effect of hydrazine exposure on polycyanurate and epoxy resin mass changes.

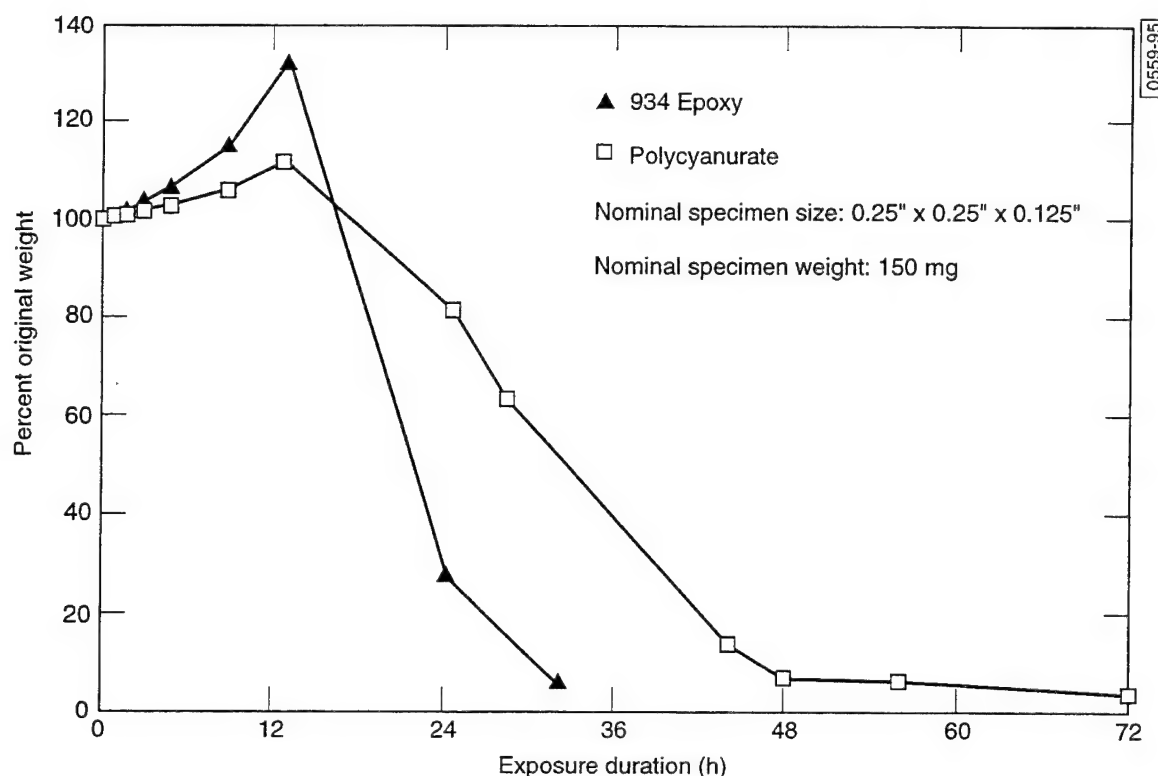
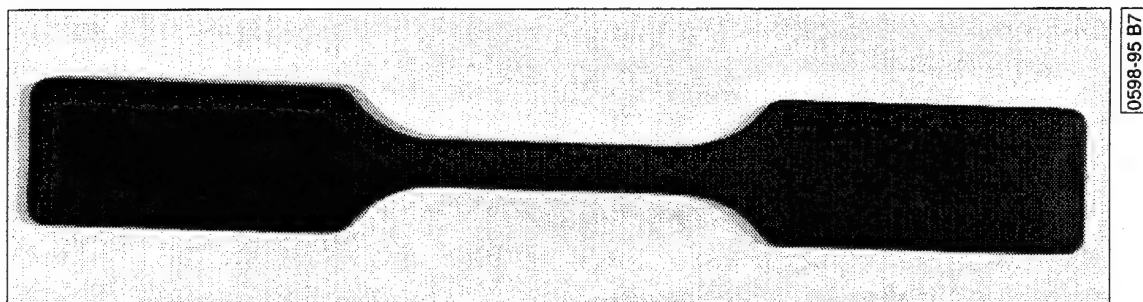


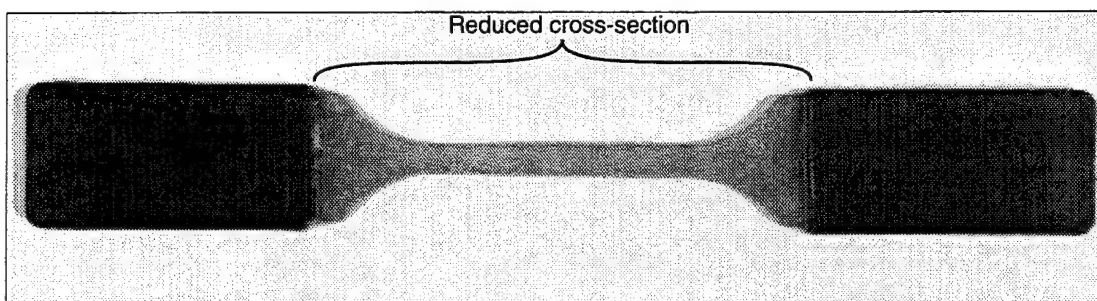
Figure 5. The effect of nitrogen tetroxide exposure on polycyanurate and epoxy resin mass changes.

oxidation behavior of both of these polymer networks. The aliphatic groups formed by the opening of the epoxide rings are likely to oxidize readily when exposed to nitrogen tetroxide. The lack of similar aliphatic groups in the polycyanurate may explain the nearly double degradation rate, or mass loss, of the epoxy compared to that of the polycyanurate.

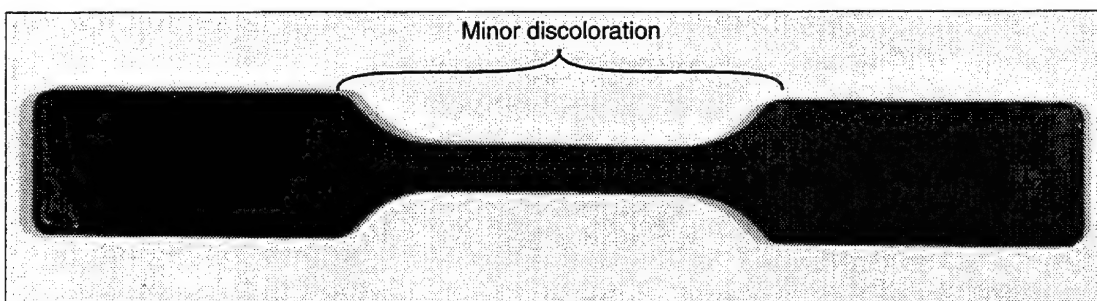
Following the mass analysis, exposed resin dogbones were subjected to tensile testing to observe variations in mechanical behavior. After a 1-h exposure to hydrazine, the strength of the polycyanurate was 10.2 ksi compared to 11.2 ksi for the control group. This accounts for only a 9% decrease in strength. However, in reality, there is a 75% reduction in the ultimate failure load. This variation between the ultimate failure stress and the ultimate failure load is entirely due to the significant mass loss of the resin after exposure, as observed from the reduced cross-sectional area in the dogbone specimens shown in Figure 6b compared to the control sample in Figure 6a. The hydrazine appears to chemically etch and remove the polycyanurate resin as a function of exposure time, without affecting unpenetrated areas. High-magnification, cross-sectional micrographs show little-to-no change in the microstructure or fracture behavior of the resultant specimens. Micro-hardness measurements were also performed across the cross-sectional area of the material to measure any physical changes. None were observed. This again is due to the fact that the rate



a. Control PC sample



b. Hydrazine exposed PC sample

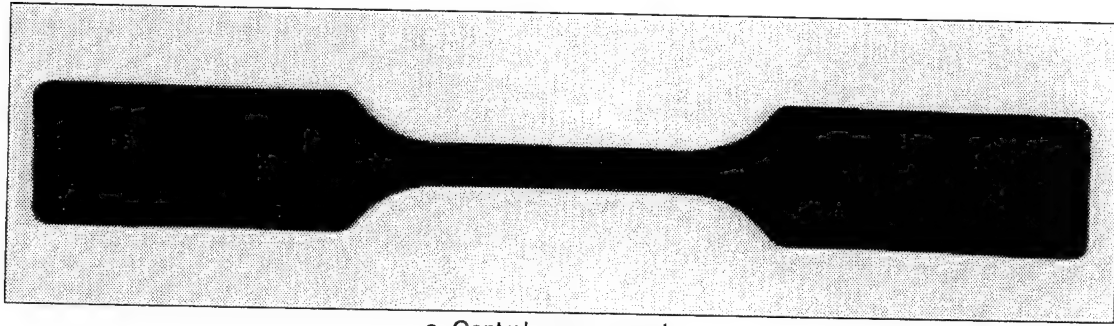


c. NTO exposed PC sample

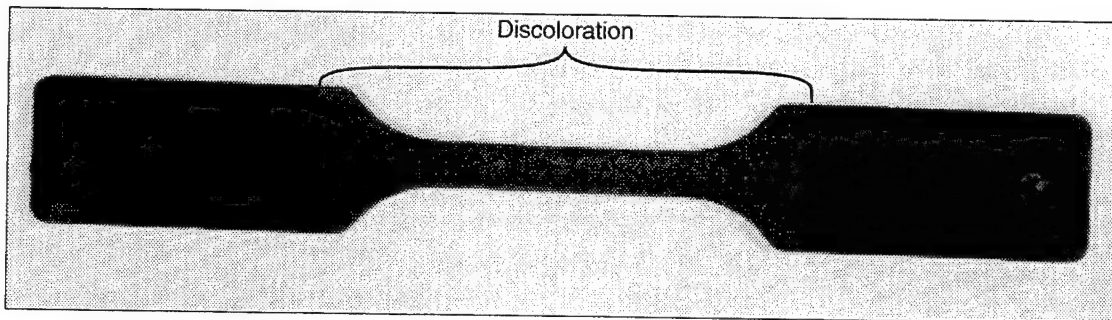
Figure 6. The effect of nitrogen tetroxide and hydrazine exposure on polycyanurate dogbone specimens.

of diffusion of the hydrazine is equal to the rate of decomposition; therefore, any material that remains for analysis has not been exposed to the fuel.

For the same exposure duration time, the strength of the epoxy was reduced by 54% to 5.2 ksi compared to 11.3 ksi for the control group. However, unlike the polycyanurate resin, the epoxy exhibited minimal mass loss, as shown in Figure 7b, compared to the control sample in Figure 7a. The strength decrease is believed to be due to the penetration of hydrazine into the polymer network. Figure 9b shows the cross-sectional fracture surface of an exposed epoxy dogbone. The light-gray area indicates the penetration depth of the hydrazine. The darker-gray area indicates the unexposed region. A clear demarcation line can be seen between both regions.

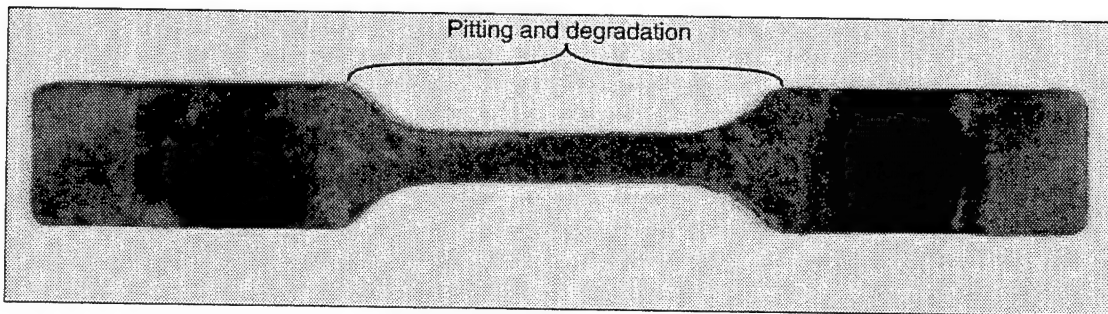


a. Control epoxy sample



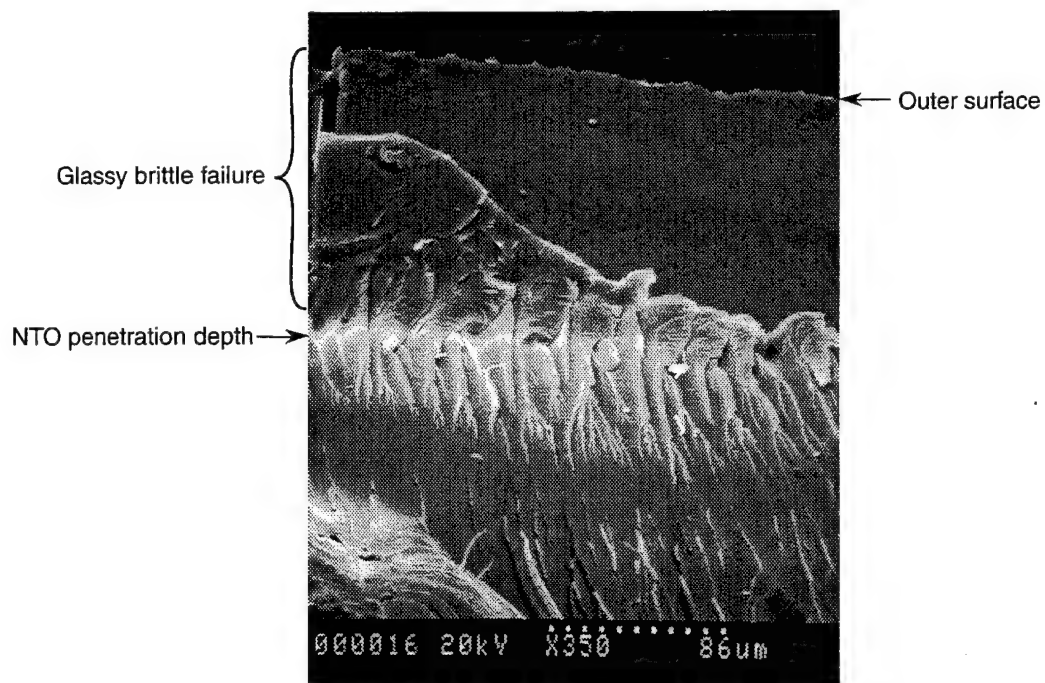
b. Hydrazine exposed epoxy sample

0593-95 B7

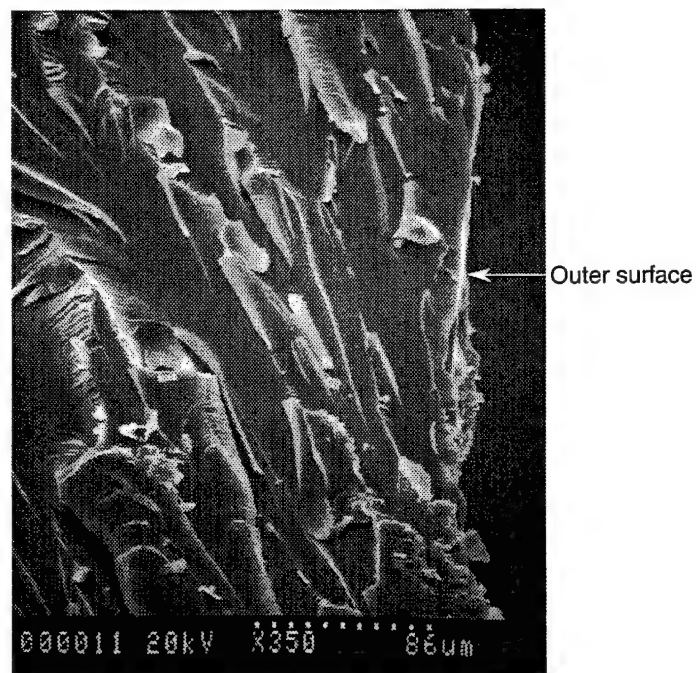


c. NTO exposed epoxy sample

Figure 7. The effect of nitrogen tetroxide and hydrazine exposure on 934 epoxy dogbone specimens.



a. NTO exposed polycyanurate resin

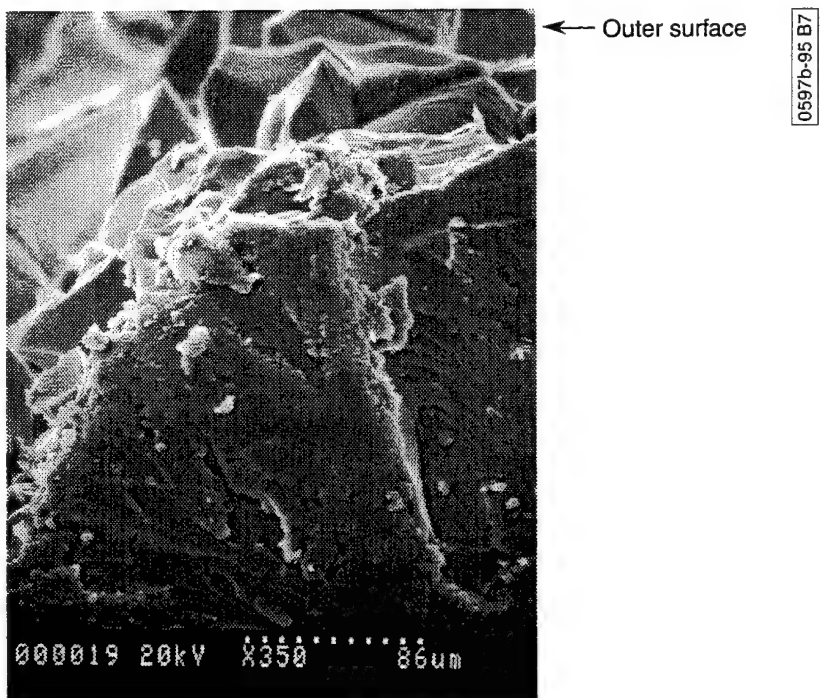


b. Hydrazine exposed polycyanurate resin

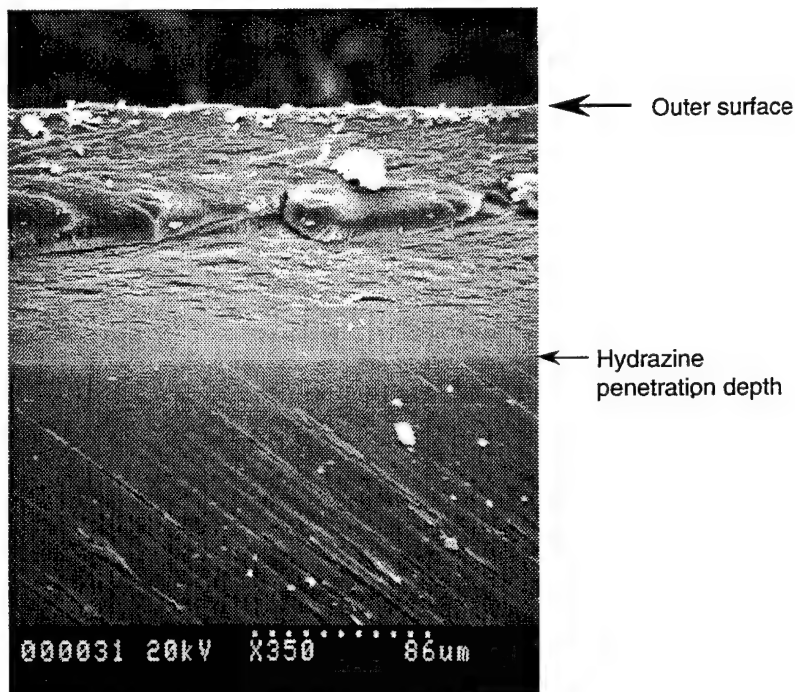
Figure 8. Scanning electron micrographs of fracture surfaces of nitrogen tetroxide- and hydrazine-exposed polycyanurate dogbone specimens.

The outer penetrated region appears to have a finer fracture structure than the remaining unexposed area. Hardness measurements across the cross-sectional area of this specimen indicate that a 38% decrease in outer surface hardness occurred as a result of a 1-h exposure in hydrazine. Unlike the polycyanurate material, the rate of diffusion is much greater than the rate of decomposition for the hydrazine-exposed epoxy specimen, as shown in Figure 9b. Thus, the dimensional changes of the material do not vary from the control sample by much, but the penetrated regions have been deleteriously affected.

As expected, both resins experienced a loss in strength due to exposure to nitrogen tetroxide. As shown after exposure to nitrogen tetroxide, the physical appearance of epoxy and polycyanurate resins are markedly different. Figures 6c and 7c show the effect of nitrogen tetroxide exposure on a polycyanurate and epoxy resin dogbone, respectively. The polycyanurate resin shows minimal observable evidence of degradation, while the epoxy sample exhibited a high degree of pitting, flaking, and discoloration. After 5-h exposures, the strengths of the polycyanurate and epoxy resin samples were reduced by 71% (3.2 ksi) and 41% (6.7 ksi), respectively. In all cases, tensile moduli of the resins were not affected, and therefore the reduced strain-to-failure observed for each condition was proportional to the reduction in tensile strength. A plot of ultimate load versus exposure duration for both propellants and resin systems is found in Figures 10 and 11. However, the effect of exposure of these resins to nitrogen tetroxide has differing results with respect to their degradation behavior. As described earlier, the rate of mass loss is greater for the epoxy than the polycyanurate resin. This is again due to the differences between the relative ratios of the rate of diffusion of the oxidizer and the rate of decomposition for the two resins. Figure 8a shows the cross-sectional fracture surface of a polycyanurate dogbone exposed to nitrogen tetroxide. The sample shown has been exposed for 5 h. The dark-gray area represents the penetrated portion of the specimen. Hardness measurements of this cross section exhibited a 24% increase in surface hardness compared to the hardness at the center. This zone of embrittlement at the outer surface caused by the nitrogen tetroxide corresponds well with the brittle planar fracture behavior of this region in comparison to the more granular ductile failure of the polycyanurate's inner cross section. On the other hand, the epoxy resin sample exposed to nitrogen tetroxide shows a rate of decomposition that is equal to the rate of diffusion and shows selective degradation as shown in Figure 9a.



a. NTO exposed epoxy resin



b. Hydrazine exposed epoxy resin

Figure 9. Scanning electron micrographs of fracture surfaces of nitrogen tetroxide and hydrazine exposed epoxy dogbone specimens.

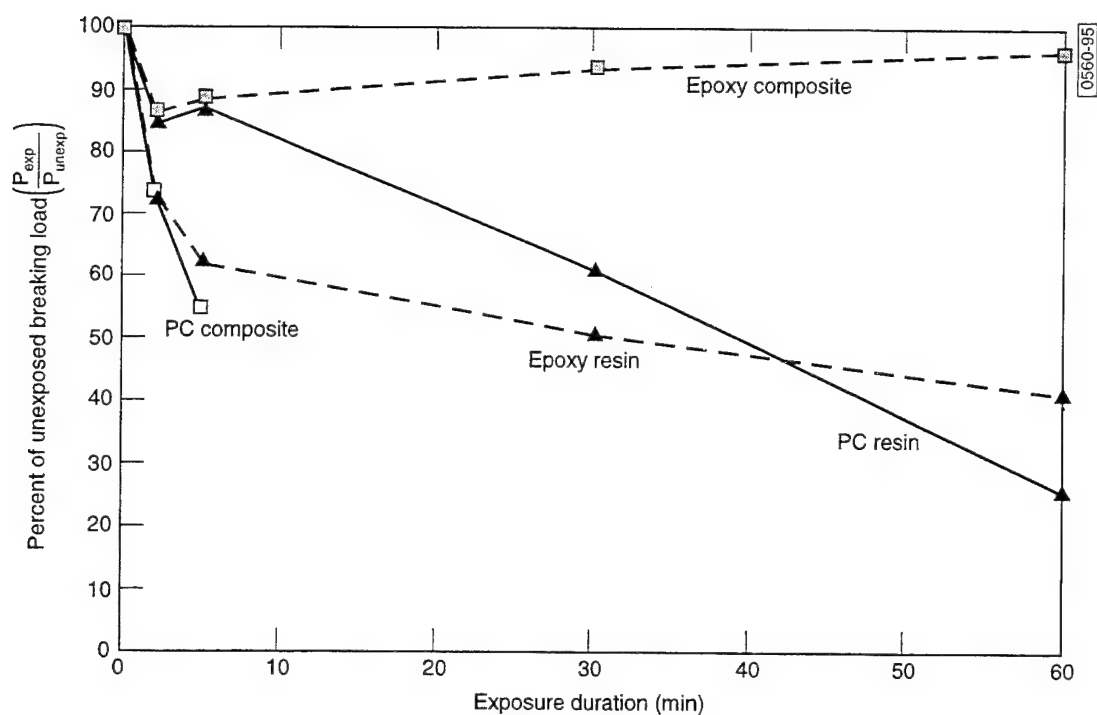


Figure 10. The effect of hydrazine exposure on polycyanurate and epoxy resin and composite samples.

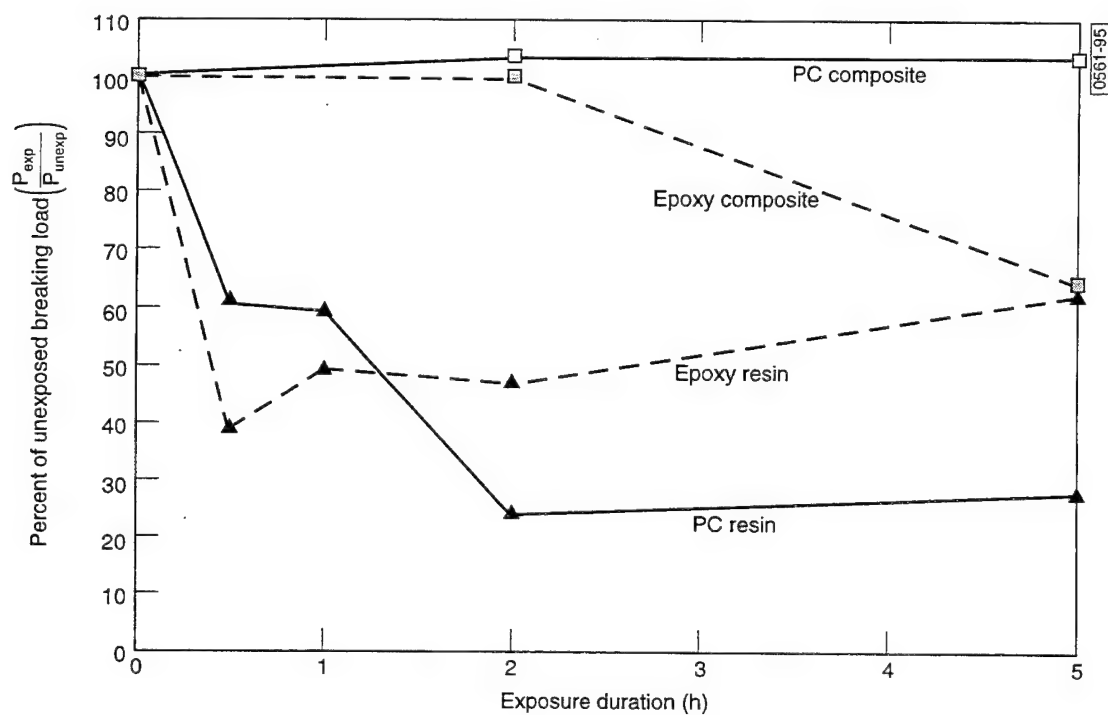


Figure 11. The effect of nitrogen tetroxide exposure on polycyanurate and epoxy resin and composite samples.

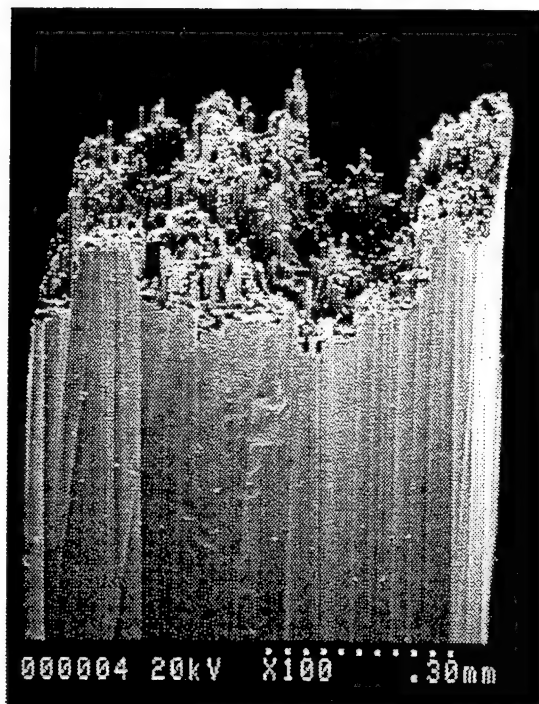
3.4 Effects of Propellants on Composite Systems

Unidirectional tow composites were also exposed to both propellants. Following exposure, these specimens were subjected to tensile testing. Figure 10 shows a plot of fiber strength utilization for the epoxy and polycyanurate composites upon hydrazine exposure. The T-300/polycyanurate composites could withstand exposures of hydrazine for up to 5 min, after which an insufficient amount of matrix remained intact to allow further testing. Specimens exposed for 5 min produced a strength of 276 ksi, a 45% strength loss, compared to 506 ksi for control specimens. Figures 12a and b show SEM micrographs of both unexposed and hydrazine-exposed unidirectional polycyanurate composites after tensile testing. As shown, the matrix material has been entirely consumed except for a small matrix core. The strength loss can therefore be attributed to the reduction of the stress transfer capabilities of the matrix material since the fiber has been shown to be resistant to hydrazine exposure.

On the other hand, the T-300/epoxy composites were exposed for as long as 1 h. After this exposure duration, the composites yielded a strength of 472 ksi, which closely compares to the 490 ksi strength of the unexposed specimens. Figures 13a and b show the fracture surfaces of unexposed and hydrazine-exposed epoxy composite. No observable matrix loss was evident as verified by resin dogbone data. The microstructural changes observed earlier on the hydrazine-exposed epoxy resin dogbones appear to have a minimal effect on the mechanical behavior of the composite. Although microstructural changes in the matrix may have occurred, these changes do not appear to have affected the bonding behavior, and thus the stress transfer capabilities, of the matrix material. The fiber-dominated strength of the composite overshadows any direct load-carrying contributions of the matrix material.

Figure 11 shows the effect of nitrogen tetroxide exposure on the strength utilization of both polycyanurate and epoxy unidirectional composites. Both of the specimen types were exposed for 2 and 5 h. T-300/polycyanurate composites did not experience any loss in strength after either exposure. However, as revealed by the mass analysis of exposed neat resin, the matrix will eventually degrade to the degree where a loss in strength will occur. Figure 12c shows the fracture surface of a polycyanurate unidirectional composite after 5 h of nitrogen tetroxide exposure. Matrix degradation has occurred at the outer surfaces of the composite, but the comparable degree of fiber pullout with the unexposed specimen indicates that the fiber-matrix interface has remained intact. The embrittlement of the matrix material also appears to have minimal effect on the composite properties. This degradation was more readily apparent with the T-300/epoxy composites, which suffered a 36% strength reduction after 5 h of exposure. Again, this occurred from mass loss of the matrix as shown in Figure 13c. The resultant strength is comparable to that of a dry fiber bundle.

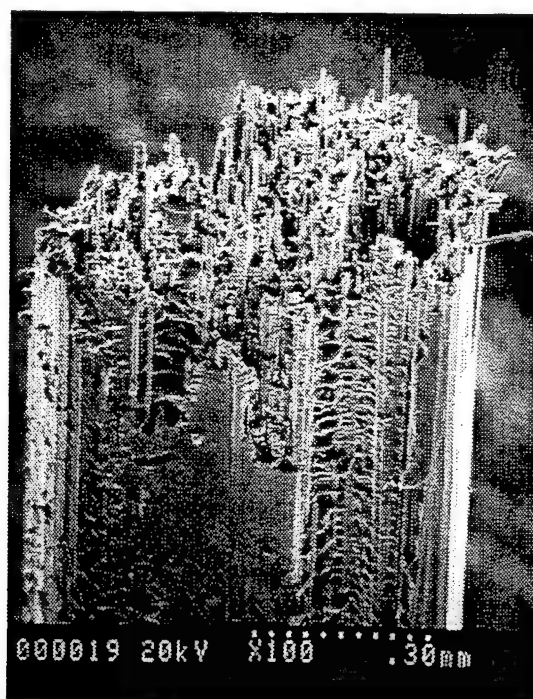
Composite panels were fabricated with a polycyanurate matrix to study propellant effects with respect to composite size. The composite panels were affected in the same manner as the unidirectional tows; however, the rate of degradation was reduced due to the decreased surface area-to-volume ratio. Five-minute hydrazine exposures yielded strength reductions of 9% and 45% for the panels and tows, respectively. Five-hour exposures to nitrogen tetroxide did not affect either composite type.



a. T-300/polycyanurate composite (control)

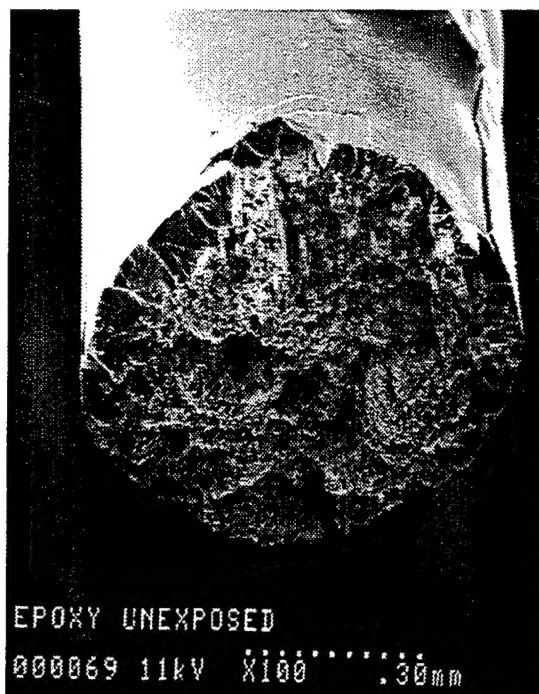


b. Hydrazine exposed T-300/polycyanurate composite



c. NTO exposed T-300/polycyanurate composite

Figure 12. Scanning electron micrographs of T-300/polycyanurate composite fracture surface as a function of exposure (a) control, (b) hydrazine exposed, (c) NTO exposed.



a. T-300/epoxy composite (control)



b. Hydrazine exposed T-300/epoxy composite



c. NTO exposed T-300/epoxy composite

Figure 13. Scanning electron micrographs of T-300/epoxy composite fracture surface as a function of exposure (a) control, (b) hydrazine exposed, (c) NTO exposed.

4. Conclusions

The T-300 PAN-based carbon fiber was unaffected by exposures to anhydrous hydrazine and nitrogen tetroxide. Tensile testing revealed no change in tensile strength as a result of the exposures. Neither propellant altered the surface of the fiber nor affected the bonding within the polymer matrices.

Both propellants have a pronounced effect on the two unreinforced resin systems. Hydrazine exposures resulted in strength reductions for both materials. The differences were related to the ratio of the rate of propellant penetration into the matrix to the rate of resin degradation. The polycyanurate resin exhibited equal rates of resin degradation and propellant diffusion. The polycyanurate resin was therefore dissolved as rapidly as the fuel diffused into the system, resulting in a small strength loss but a significant reduction in ultimate load. The epoxy reacted differently because the rate of penetration was greater than the rate of degradation. The defects resulting from degradation caused a reduction in strength. Both materials were degraded by nitrogen tetroxide. The oxidizer attacked the surface of the resins, was absorbed, and eventually consumed them. The degradation introduced flaws into the materials, which led to premature failure of the resin specimens.

Composite specimens fabricated using each resin system retained the majority of their load-carrying capability until mass loss of the matrix was experienced. A significant mass loss was observed for polycyanurate matrices exposed to anhydrous hydrazine and epoxy matrices exposed to nitrogen tetroxide. This reduction in the stress transfer capability did not allow the composite to fully utilize the strength of the reinforcing fibers. Conversely, polycyanurate matrices were less susceptible to degradation by the oxidizer, as were epoxy matrices when exposed to the fuel. As a result, the integrity and stress transfer capability of the matrices were maintained, allowing the composites to maintain properties near those of the unexposed specimens. Any flaws introduced into the resins by reaction with the propellants were mitigated by the reinforcing fibers, which served to disrupt crack propagation.

Polycyanurates appear very promising for spacecraft structural applications and offer numerous benefits over current state-of-the-art epoxies. While extended exposure of these two types of composite systems to hypergol propellants is not recommended, it is clear from this study that epoxy composites offer better resistance to anhydrous hydrazine, and polycyanurate composites afford more protection against nitrogen tetroxide.

References

1. Zakrzewski, Mazenko, Peters, and Dean, "Tomorrow's Materials: Today," Society for the Advancement of Material & Process Engineering (SAMPE), Covina, CA 91722; Vol. 34, Book 1 of 2, 1989.
2. International Encyclopedia; Stuart M. Lee; VCH Publishers Inc., New York, NY; 1990.
3. Composite Materials: Testing & Design (Fifth Conference); S.W. Tsai; American Society for Testing & Materials, Philadelphia, PA 19103; 1979.
4. Sax and Lewis; Condensed Chemical Dictionary; Van Nostrand Reinhold, New York, NY; 1987.
5. Engineered Materials Handbook: Composites; ASM International, Ohio; 1987.
6. USAF / COPV Program Test Plan, Subtask 3.6, Materials Compatibility Testing of Graphite/Epoxy Composite Overwrap Pressure Vessels (COPVs); NASA, Lyndon B. Johnson Space Center; April 1993.
7. J. Kilduff, D. D. Davis, and L. Linley, The Evaluation of Materials Compatibility with Aerospace Fluids, NASA White Sands Test Facility, September 1991.
8. High Modulus Fiber Reinforced Prepreg Development: Material Assessment and Benefits Analysis, December Technical Report, Hughes Space and Communications Company for Wright Laboratory - Materials Directorate, December 1993.
9. Institute for Defense Analysis, Polycyanurate Symposium, June 1993.
10. Tsai and Hahn; Introduction to Composite Materials; Technomic Publishing Company, Inc, Lancaster, PA 17604; 1980.
11. American Society for Testing & Materials (ASTM) standards:
 - (1) D638-91 Tensile Properties of Plastics
 - (2) D3039-76 Tensile Properties of Fiber-Resin Composites
 - (3) D4018-81 Tensile Properties of Continuous Filament Carbon and Graphite Yarns Strands, Rovings, and Tows
12. Military specifications:
 - (1) MIL-P-26536C, 25 Jul 74, Hydrazine
 - (2) MIL-P-26539D, 28 Aug 89, Nitrogen Tetroxide
13. Material information from Amoco Performance Products, Ciba-Geigy, ICI Fiberite, and YLA.
14. D. A. Shimp, Thermal Performance of Cyanate Functional Thermosetting Resins, SAMPE Quarterly, Volume 19, No. 1, October 1987.
15. D. A. Shimp, The Translation of Dicyanate Structure and Cyclotrimerization Efficiency to Polycyanurate Properties, American Chemical Society Meeting, April 1986.

TECHNOLOGY OPERATIONS

The Aerospace Corporation functions as an "architect-engineer" for national security programs, specializing in advanced military space systems. The Corporation's Technology Operations supports the effective and timely development and operation of national security systems through scientific research and the application of advanced technology. Vital to the success of the Corporation is the technical staff's wide-ranging expertise and its ability to stay abreast of new technological developments and program support issues associated with rapidly evolving space systems. Contributing capabilities are provided by these individual Technology Centers:

Electronics Technology Center: Microelectronics, VLSI reliability, failure analysis, solid-state device physics, compound semiconductors, radiation effects, infrared and CCD detector devices, Micro-Electro-Mechanical Systems (MEMS), and data storage and display technologies; lasers and electro-optics, solid state laser design, micro-optics, optical communications, and fiber optic sensors; atomic frequency standards, applied laser spectroscopy, laser chemistry, atmospheric propagation and beam control, LIDAR/LADAR remote sensing; solar cell and array testing and evaluation, battery electrochemistry, battery testing and evaluation.

Mechanics and Materials Technology Center: Evaluation and characterization of new materials: metals, alloys, ceramics, polymers and their composites, and new forms of carbon; development and analysis of thin films and deposition techniques; nondestructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; development and evaluation of hardened components; analysis and evaluation of materials at cryogenic and elevated temperatures; launch vehicle and reentry fluid mechanics, heat transfer and flight dynamics; chemical and electric propulsion; spacecraft structural mechanics, spacecraft survivability and vulnerability assessment; contamination, thermal and structural control; high temperature thermomechanics, gas kinetics and radiation; lubrication and surface phenomena.

Space and Environment Technology Center: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation; propellant chemistry, chemical dynamics, environmental chemistry, trace detection; atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiative signatures of missile plumes, and sensor out-of-field-of-view rejection.